Historical use of lead arsenate insecticides, resulting soil contamination and implications for soil remediation

PERYEA Francis J.

Tree Fruit Research and Extension Center, Washington State University, Wenatchee, Washington, USA

Arsenical insecticides have been used in agriculture for centuries. The earliest available records indicate use of arsenic sulfides in China as early as A.D. 900, and incorporation of arsenic oxide in ant bait in Europe in 1699 (Shepard, 1939). The first insecticidal use of the copper acetoarsenite pigment commonly known as Paris green [$(CH_3COO)_2Cu.3Cu(AsO_2)_2$] appears to have been in 1867 on Colorado potato beetle in the USA. Paris green sprays were soon adopted by fruit growers for control of codling moth (*Cydia pomonella*) in apple, a use that continued through about 1900. Paris green also was used internationally for mosquito abatement, where it was applied directly to water bodies as a powder or mixed with moist sand, as well as for control of other insects.

Lead arsenate (LA) was the most extensively used of the arsenical insecticides. It was first prepared as an insecticide in 1892 for use against gypsy moth (*Lymantria dispar*) in Massachusetts, USA. Paris green was found to be very phytotoxic at the rates required for gypsy moth control, a problem largely alleviated by the lower solubility of LA. Lead arsenate applied in foliar sprays also adhered well to the surfaces of plants, so its pesticidal effect was longer lasting. These properties were useful to farmers, with the consequence that LA was rapidly adopted for insecticidal use throughout the world. Lead arsenate initially was prepared by farmers at home by reacting soluble lead salts with sodium arsenate, a practice that continued in some countries through the 1930s and likely 1940s. Lead arsenate pastes and powders also were sold commercially. Their formulations became more refined over time and eventually two principal forms were marketed: basic lead arsenate [$Pb_5OH(AsO_4)_3$] for use in certain areas in California, USA, and acid lead arsenate [$PbHAsO_4$] for all other locations.

Lead arsenate insecticide was used in Australia, Canada, New Zealand, and the USA (Peryea and Kammereck, 1997). It also was used in England (Gratwick, 1965), and was the principal arsenical pesticide used in France and also was used in North Africa (Balachowsky and Mesnil, 1936). Lead arsenate likely was used in many other countries, particularly where codling moth was a pest of apples. It also was used for insect pests of other fruit tree species, garden crops and turfgrasses, and for mosquito abatement (Shepard, 1951), in cattle dips (R. Naidu, CSIRO, Adelaide, Australia, personal communication), and on rubber and coffee trees (FCH, 1986).

Until the First World War, only minor amounts of calcium arsenate were used as pesticides (Shepard, 1939). During the war, the price of Pb salts became very high. Because of its lower relative cost, calcium arsenate replaced the more expensive LA for several uses, particularly control of boll weevil (*Anthonomus grandis*) in cotton and for forest insect pests. Lead arsenate remained the preferred insecticide for codling moth control because of its greater efficacy and lower phytotoxicity. Calcium arsenate use was reported in the USA and Peru (Shepard, 1939) and it was particularly popular in Germany (Balachowsky and Mesnil, 1936). Aluminum arsenate insecticides were developed and used in France during the 1930s (Balachowsky and Mesnil, 1936). A variety of other metal arsenates and arsenites were experimentally evaluated or used on a limited commercial basis during the past century (Shepard, 1939).

The search for substitutes for LA began in earnest when it was discovered in 1919 that contemporary practices for washing produce were failing to adequately remove As residues (Shepard, 1939). Unfortunately, all of the tested alternative materials were found to provide less effective insect control or were more toxic to plants and animals. No adequate substitutes were found until 1947, when the synthetic organic insecticide dichlorodiphenyltrichloroethane (DDT) was introduced.

Lead arsenate use in Washington State, USA, effectively terminated in 1948, when DDT became widely available to the public (Benson et al., 1968). By that time, the principal target pest, codling moth, had developed resistance to the arsenate compound, and DDT was found to be a much more effective control agent. Veneman et al. (1983) stated that LA use ceased in Massachusetts, USA, in the early 1950s. The partial or complete substitution of DDT for LA appears to have been a general phenomenon. When LA use did continue, it was applied at much lower rates in combination with DDT and other insecticides (Frank et al., 1976b). Continuing pesticidal use of LA in the USA was documented in New York through 1965 (Aten et al., 1980) and Michigan, Pennsylvania, and Georgia during the mid-1960s (Steevens et al., 1970). All insecticidal uses of LA in the USA were officially banned on 1 August 1988 (USEPA, 1988), with a comment that all registrations for insecticidal use had lapsed before that date.

In Canada, LA sprays were officially recommended for use in Nova Scotia apple orchards at least as late as 1965 (Bishop and Chisholm, 1966) and in Ontario apple orchards at least as late as 1975 (Frank et al., 1976a). It was still

being applied for apple maggot (*Rhagoletis pomonella*) control in New Brunswick in 1965 (Maxwell et al., 1965) and in Nova Scotia as late as 1981 (MacLean and Langille, 1981). The data of Boppel and Diehl (1993) indicated that Pb and As concentrations in German home-canned cherry preserves declined after about 1960, suggesting cessation of LA use. Nagy (1974) stated that arsenical pesticide use in Germany was effectively banned by 1974 and presented fruit analyses which supported reports that arsenical sprays were still being used in French apple orchards at that time. Merry et al. (1983) stated that commercial use of LA decreased in Australia after the introduction of DDT in 1950, and that the insecticide was not used on exported crops in 1983. According to Pocklington and Tatton (1966), LA use in apple orchards was officially recommended in New Zealand and the United Kingdom at least through 1966, particularly where the target pests had developed resistance to other insecticides. Failure of recent publications to comment on the topic suggests that LA use on food crops is now discontinued or banned in most countries.

Frequent applications of LA at increasing rates over time eventually caused Pb and As to accumulate in topsoil. Handgun sprayers were used to apply aqueous slurries of LA to individual trees, resulting in extreme variability in the horizontal distribution of soil Pb and As enrichment (Veneman et al., 1983). Soil loading with LA also varied with time, with LA use and rate depending on the species and population sizes of insect pests and their resistance to arsenical poisoning, the species and size of the trees, the presence of fruit on the trees (codling moth is a direct pest of fruits - no fruit means no need for pesticide), and use of alternative pesticides. Point contamination of soil with Pb and As around cattle dips also has been reported (R. Naidu, personal communication).

Many studies conducted have concluded that intra-soil redistribution of Pb and As derived from LA sprays is limited. Snyder (1935) cited differential crop growth in potted topsoils and subsoils as indirect evidence that As residues were confined to the topsoil. Vandecaveye et al. (1936) reported that HNO3-extractable As concentrations in the top 15 cm of four soils were 2.5 to 6.5 times higher than in the 15- to 30-cm depth increments. Similarly, Jones and Hatch (1937) found that total Pb and As concentrations in the top 20 cm of soil in 21 commercial orchards were substantially higher than in the 20- to 40-cm depth increments. They concluded that redistribution of surface-applied Pb and As within orchard soils was limited to the depth of mechanical mixing caused by tillage implements. Overley (1950) concluded that phytotoxic levels of As were restricted to the top 10 cm of soil in apple orchards. Aten et al. (1980) concluded that all of the Pb and As derived from LA sprays was contained in the top 25 cm of an apple orchard sprayed with LA between 1929 and 1965. Veneman et al. (1983) reported no enrichment of Pb and As below the 25-cm soil depth in a LA-contaminated apple orchard. The Pb/As concentration ratio decreased with depth within the top 25 cm of soil, implying greater downward movement of As relative to Pb.

Several studies have reported substantial downward movement of As in LA-contaminated soils. Merry et al. (1983) found no apparent redistribution of Pb but considerable movement of As into the subsoils of six soils. In a survey of ten orchard soils, Veneman (1985) indicated that total Pb concentrations were highest at the soil surface, remained fairly high throughout the surface horizon, and generally dropped sharply in the subsoil. He also reported that As showed some evidence of translocation, particularly in sandy soils. Arsenic in one sandy soil, estimated at about 160 kg/ha, had been completely leached out of the soil profile. Benson et al. (1968) observed apparent As enrichment in the 2- to 3-foot depth increment of 25% of the orchard soils sampled in a fruit-growing area. Peryea and Creger (1994) found that the highest concentrations of Pb and As were present in the top 20 cm of minimally disturbed LA-contaminated soils; however, there was substantial downward migration of both Pb and As with the latter element exhibiting greater relative movement. Arsenic enrichment was observed to depth of 125 cm (the deepest depth sampled) in three of the six study soils. Elfving et al. (1994) also reported greater mobility of As than Pb in LA-contaminated soils.

In general, plants do not absorb appreciable amounts of Pb and As and translocate these elements to edible plant tissues, a phenomenon termed the "soil-plant barrier" (Chaney and Ryan, 1994). Lead in LA-contaminated soils is not appreciably phytotoxic (Overley, 1950). The concentration of Pb in tree fruits grown on LA-contaminated soils is extremely low (Creger and Peryea, 1992). In contrast, the Pb concentration in vegetable crops is higher, and in some leafy and tuberous plants can approach or exceed values associated with human health risk (Chisholm, 1972; Aten et al., 1980). High-Pb soil particles adhering to the surfaces of these plants may account for some of the elevated Pb content. Arsenic in LA-contaminated soils is phytoavailable (Creger and Peryea, 1992; Peryea, 1998) and can be phytotoxic (Benson 1976; Merwin, 1994). While elevated compared to crops grown on uncontaminated soils, the concentrations of As in tree fruits and the edible portions of garden crops grown on LA-contaminated soil are substantially lower than levels associated with human health risk (Jones and Hatch, 1945; Chisholm, 1972; Creger and Peryea, 1992).

Thermodynamic considerations and empirical evidence suggest that LA is not stable in soil environments and will convert over time to less soluble mineral forms. Differential intra-soil movement of Pb and As suggests that the LA has undergone at least partial hydrolysis and the two elements may no longer be chemically associated in

soil. Although Hess and Blanchar (1976) concluded that dissolved Pb concentrations were consistent with possible control by LA in two LA-contaminated soils from Missouri, USA, a more recent study suggests that the LA-derived Pb has converted to less soluble Pb-hydroxide or phosphate minerals (Kalbasi et al., 1995). Arsenic freshly added to soil becomes less easily extracted over time (Jacobs et al., 1970), consistent with indirect evidence suggesting that As in LA-contaminated soil has become less phytoavailable and phytotoxic since LA was last added to the soil (Merry et al., 1986; Peryea, 1998).

The simultaneous presence of Pb and As in LA-contaminated soils, coupled with probable As enrichment of subsoil, greatly complicates remediation possibilities. In addition, many of the contaminated sites occur in former rural locations that are undergoing urbanization, particularly residential development. A variety of remediation strategies have been employed or proposed (Lange and Thomulka, 1994). Removal of the Pb and As is usually the preferred regulatory solution. Engineering controls such as encapsulation may be acceptable. Dilution by mixing with uncontaminated soils often is not considered acceptable. *In situ* chemical stabilization may be acceptable in some cases but is usually not considered a permanent solution, and is obviated if soil cleanup thresholds are based on total rather than bioactive concentrations of the contaminants.

Physical removal of contaminated topsoil by excavation has been carried out in Washington, USA. The economic cost is very high, with estimates ranging from US$25,000 to US$1 million per acre, depending on the depth to which soil is removed and the availability of a disposal site. This strategy is further complicated by the infertility of the exposed subsoils and the lack of adequate amounts of replacement topsoil.

Several procedures are employed for soil encapsulation. Covering the contaminated soil with buildings and layers of concrete and asphalt is suitable for industrial and commercial land uses and can be used for portions of residential and school sites. Encapsulation with imported uncontaminated soil has also been used; however, this practice is expensive and may be limited by soil availability. The new topsoil is subject to physical disturbance by humans, burrowing animals and solifluction which can re-expose the contaminated subsoil. At sites where plants are grown, subsoil Pb and As may be absorbed by roots and translocated to shoots and leaves which eventually will die and return some of the original contaminants back to the soil surface. Encapsulation by maintaining a continuous grass turf surface is acceptable for some circumstances by several regulatory agencies (Lange and Thomulka, 1994).

Incorporation of soluble phosphorus (P) compounds has been proposed as a strategy to reduce Pb solubility in Pb-contaminated soils by the *de novo* formation of pyromorphite minerals [$(Pb_5(PO_4)_3X$ where x=halide or hydroxide] (Ruby et al., 1994). The effectiveness of this strategy applied to LA-contaminated soils is variable (Kalbasi et al., 1995; Ma and Rao, 1997), possibly because pyromorphite minerals already may have been formed since LA was last applied to the soil. Furthermore, in contrast to Pb, the effect of added P is to increase the solubility of soil As in LA-contaminated soil through a mechanism of competitive anion exchange (Peryea, 1991). This process temporarily increases soil As phytoavailability (Peryea, 1998) and intra-soil mobility (Peryea and Kammereck, 1997). In the latter case, apparent preferential adsorption of P by the uncontaminated subsoil effectively prevents resorption of As and forces it to translocate to even greater depths as both elements simultaneously leach downwards into the soil. The environmental consequences of P addition to LA-contaminated soils therefore are equivocal - the added P may reduce Pb bioavailability and total As content in the topsoil; however, redistribution of As into the subsoil may enhance risk of ground water contamination.

Lead and As bioavailability also may be reduced by addition of hydrous iron oxides and organic materials to contaminated soil (Chaney and Ryan, 1994); however, these techniques have not been evaluated on LA-contaminated soil. Soil As is subject to microbially mediated conversion to volatile alkylarsines (Gao and Burau, 1997). Unfortunately, the amount of As evolved from LA-contaminated soils is too low to be of remedial significance, while logistical problems preclude implementation of microbial bioremediation ικn the field (Peryea, 1991).

In summary, use of LA insecticide was an internationally accepted practice adopted because of its effective control of insect pests and its low phytotoxicity compared to its contemporaneous alternatives. Attempts to find suitable substitutes for LA were unsuccessful until the development of synthetic organic insecticides which became generally available following the Second World War. Limited insecticidal use of LA continued after that time in some areas. Use of LA on agricultural crops currently is banned in some countries. Remediation of LA-contaminated soils is made difficult by the widespread areal extent of contamination, possible subsoil enrichment with As, and the differing physicochemical behaviors of Pb and As in soil. Keeping LA-contaminated soils in orchard production effectively limits human exposure to Pb and As, while conversion of LA-contaminated land from agricultural to other uses, particularly residential development, substantially enhances the likelihood that humans will be exposed to these elements. The cost, logistical problems, and impermanence of current remediation strategies and practices limit their implementation and effectiveness on LA-contaminated soils.

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